

Engineering Case Reports

Effectiveness of Local Exhaust Ventilation (LEV) in Controlling Engineered Nanomaterial Emissions During Reactor Cleanout Operations

INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) is the federal agency that conducts research and makes recommendations for preventing work-related injuries, illnesses, and deaths. The NIOSH Nanotechnology Research Center coordinates the Institute's laboratory, field, and information dissemination activities on the development of tools, practices, and recommendations for the guidance document *Approaches to Safe Nanotechnology* (<http://www.cdc.gov/niosh/topics/nanotech/safenano/>). A key input to the development of that document is field research studies. The NIOSH nanotechnology field research team has the objective of characterizing processes where engineered nanomaterials are produced or used. To do this, the field team

- evaluates the entire material flow of a process and identifies points of potential material emission that can result in worker exposure;
- uses an array of instruments and conventional air sampling methods to characterize exposures;
- evaluates engineering controls and their effectiveness in reducing emissions and exposures;
- evaluates work practices used during the production or use of engineered nanomaterials;
- evaluates the use of personal protective equipment in use, if any, including respiratory protection.

BACKGROUND

There is limited published information on the potential adverse occupational health effects of engineered nanomaterials (ENM)⁽¹⁾ man-made material possessing at least one size dimension between approximately 1 to 100 nm), but results from laboratory animal studies on novel engineered nanoparticles do generate reasons for concern.⁽²⁾ In addition, the nanometer form of some familiar materials demonstrates heightened biological reactivity in similar tests.⁽³⁾ Uncertainties concerning exposure risk may be great because the ENM characteristics may be quite different from those of larger particles with the same chemical composition. The most likely route of exposure to engineered nanomaterials is through inhalation.⁽⁴⁾ However, ingestion or dermal penetration may also occur.^(5–7) Unfortunately, there are currently no occupational exposure limits governing workplace exposure to ENMs specifically

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to their existence as nanoparticles. For these reasons ENMs present new challenges to understanding, predicting, and managing potential health risks to workers.⁽¹⁾

Recent toxicological studies have indicated that dose metrics other than mass concentration (mg/m^3) may be a better measure when evaluating the health effects of exposure to nanoparticles. Currently, a variety of commercially available air sampling instrumentation exists that can characterize nanoscale aerosols based on a number of metrics (mass, number concentration, size distribution, surface area, etc.). However, none are small enough to be worn by workers and, in turn, allow the estimation of ENM concentration in their personal breathing zone. Others have recognized this limitation and have attempted to characterize nanoscale aerosols in ambient air, using a variety of instruments, within different task and process areas in a diverse set of workplaces to provide an indication of “potential” worker exposure.^(8–10)

In January 2007, NIOSH received a request from the management team of an engineered nanoparticle-producing company to be a volunteer participant in a NIOSH field research study to evaluate process-specific emissions during the production of ENMs. The ENMs of interest consisted solely of metal and metal alloy spheres of approximately 15–50 nm in diameter. An initial baseline assessment of work practices, existing engineering controls, personal protective equipment (PPE), and potential sources of ENM emissions was conducted in February, 2007. Based on the findings of the initial baseline assessment, it was determined that during a specific operation (reactor cleanout of slag and waste using brushes and scrapers), ENMs were released to the production area atmosphere and, in turn, could result in potential worker exposure. This finding prompted the company to purchase a portable, local exhaust ventilation (LEV) unit commonly used during welding processes to capture fumes in an attempt to control ENM emissions. The unit consisted of a 15 cm diameter, flexible, flanged duct attached to a high-efficiency particulate air (HEPA) filtered air handler equipped with a carbon pre-filter and was designed to operate at a flow rate of $28.3 \text{ m}^3/\text{min}$ (Figure 1). In July 2007, NIOSH returned to the facility and used the same real-time, direct-reading instrumentation and filter-based air samples employed in the baseline assessment to determine the effectiveness of the newly implemented control technology.

Process Description

The company, which was founded in 2002, is engaged primarily in the production of nanoscale metal catalytic materials, such as manganese, nickel, and cobalt via gas-phase condensation. These materials are used in the production of energy efficient batteries, fuel cells, and photovoltaic devices, to name a few. Currently, the process used for creating the nanoscale materials is in the research and process development phase, with a long-term goal of large-scale commercialization of the process and equipment. The 697 m^2 facility, which produces approximately one kg of material per day, consists of a production area, two laboratories, and an office area. Two

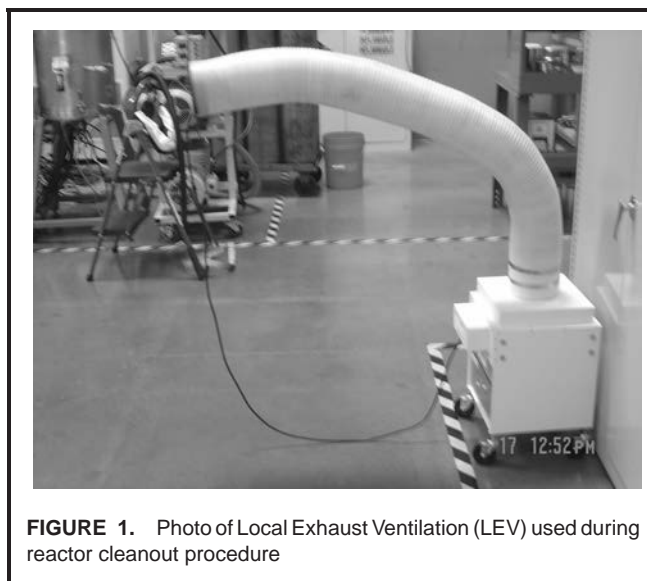


FIGURE 1. Photo of Local Exhaust Ventilation (LEV) used during reactor cleanout procedure

production technicians operate four process reactors. Each technician works an 8-hr shift, 5 days a week. PPE used by the technicians during reactor cleanout consisted of a full-body Tyvek suit, nitrile gloves, wrist-to-elbow cotton arm covers, and a 3M L-122 full-face, positive pressure airline respirator.

The principle of operation of the gas-phase condensation vapor deposition reactor is as follows: Elemental metal in bulk powder form (approximately $150 \mu\text{m}$ in diameter) is loaded into a hopper that feeds a ceramic tray that is electrically heated inside a vacuum reactor containing a mixture of an inert gas (argon) and oxygen. The metal becomes molten, then gaseous, and slowly condenses to produce nanoscale metal oxide spheres. The spheres are generated as the gaseous metal condenses and deposits onto the walls of the reactor. A motorized, mechanical scraper removes the deposited nanospheres from the reactor wall where they are collected via gravity in a sealed polycarbonate jar at the bottom of the reactor. The time needed to fill a jar with approximately 200 grams of material is 2 hr. The exhaust from the reactor, which contains particulate and an inert gas/oxygen mixture, is treated via an inline 600 mesh screen ($9 \mu\text{m}$ particle size) followed by an oil mist eliminator prior to discharge to the production area atmosphere. The volume of air contained within the production area was reported to be 3217 m^3 . General plant exhaust ventilation (which was not operating at the time of either survey), consists of two rooftop exhaust fans (flow rate = $57 \text{ m}^3/\text{min}$ each) and a roll-up type garage door. The purpose of this ventilation system is to provide temperature control of the plant environment. During warm weather, employees reported that they opened the garage door and activated the rooftop exhaust fans. When this occurred, a rate of two air changes per hour (ACH) was achieved.

METHODS

To evaluate the effectiveness of the LEV system in controlling the release of ENMs, area air samples were collected



FIGURE 2. Reactor cleanout process with no fume extractor (LEV)

with and without LEV for the duration of the reactor cleanout process (Figures 2 and 3). All air samplers (filter-based and direct-reading instruments) were positioned at the rim of the opening of the reactor (Figure 2) and opposite the inlet of the LEV (Figure 3) with the intention of approximating a worst case potential exposure scenario. In addition, a general area air sample was collected in the center of the production area before any ENM-generating activities began to serve as an indicator of background concentrations not related to the reactor cleanout process. Filter-based samples were collected using Leland Legacy (SKC Inc., Eighty Four, Pa.) pumps at a sampling rate of 7.0 L/min.

Pumps were calibrated before and after each day of sampling. Air samples to determine mass concentration of specific

elements used to create ENMs were collected on 37 mm diameter, 0.8 μm pore size, open-face mixed cellulose ester (MCE) membrane filters and analyzed according to *NIOSH Manual of Analytical Methods (NMAM) Method 7302*.⁽¹¹⁾ A duplicate set of air samples was collected alongside the mass-based air samples and analyzed using transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS) capability. TEM with EDS allows the microscopist to identify particles in the nanometer size range, morphology of the particles (size, shape, degree of agglomeration), and elemental composition. Filter-based air sampling times ranged from 10 min to 30 min (volume of air sampled ranged from 70 L to 210 L) and was dependent on the time necessary to complete the reactor cleanout process.

In addition to the filter-based air sampling, two direct-reading, real-time instruments were used to characterize emissions, with and without LEV, during the reactor cleanout process. To maintain consistency with the filter-based air sampling effort, the sampling inlet of each direct-reading instrument was positioned adjacent to the filter-based air sampling media. The first instrument was a TSI model 3007 (TSI, Inc., Shoreview, Minn.) handheld condensation particle counter (CPC). The CPC operates by drawing air through a size-selective inlet, passing it through a heated saturator filled with isopropyl alcohol and then cooling the airstream via a condenser chamber. In the condenser, the alcohol vapors condense on the particles and are passed through an optical detector where they are counted. The CPC unit measures particles in the size range of 10 to 1000 nm. The data output is expressed as total number of particles per cubic centimeter of sampled air with an upper dynamic range limit of approximately 100,000 particles per cubic centimeter of air. The value of this instrument for evaluating ENM emissions is its ability to detect particles in the 10 to 100 nm range,



FIGURE 3. Typical location of fume extractor and production operator during reactor cleanout activities (filter-based air sampling devices located in upper left corner of photo on left)

even though it will respond to the presence of larger particles. A second direct-reading, real-time instrument was used to determine the concentration of particulates based on optical counting principles using laser light scattering (HHPC-6, ART Instruments, Grants Pass, Ore.). This instrument can measure the total number of particles per liter of air within six specific size ranges: 300–500 nm; 500–1000 nm; 1000–3000 nm; 3000–5000 nm; 5000–10,000 nm; and > 10,000 nm.

Because the size of singular and agglomerated ENMs often varies, it was determined that using these particle sizing and counting instruments would provide a qualitative indication of the concentration of both species. For example, a high particle count on the CPC, in combination with a high particle count in the small size range (300–500 nm) on the HHPC, would indicate the possible presence of ENMs. Conversely, a low CPC count, in combination with a high HHPC count in the larger size range (> 1000 nm), would indicate the presence of larger particles or highly agglomerated ENMs.

Because these two instruments cannot distinguish between specific types of particulate matter (e.g., road dust vs. metal oxide spheres), background particle number concentration measurements were made before and after the work shift in the reactor area. No local exhaust ventilation was used during the background particle number concentration measurements. The “before and after” background particle number concentration data were averaged and then subtracted from the “process-specific” measurements to calculate an “adjusted concentration.” The adjusted concentration will serve as an indicator of particulate matter emitted during reactor cleanout.

RESULTS

The ENMs manufactured during this site visit consisted of oxides of manganese, cobalt, and silver, with each in a separate reactor. Three pairs of filter-based area air samples (mass and TEM) were collected during each reactor cleanout

process. One set of filters was collected in the production area (near the reactors) prior to commencing the cleanout process to serve as an indicator of workplace background concentrations. None of the metal oxides in production were detected on the background sample.

Air concentrations for the three metal oxides when no LEV was used during reactor cleanout ranged from 710 $\mu\text{g}/\text{m}^3$ to 6700 $\mu\text{g}/\text{m}^3$. However, air concentrations measured on a different day when the LEV was operating were substantially lower and ranged from 41 $\mu\text{g}/\text{m}^3$ to 1700 $\mu\text{g}/\text{m}^3$ (Table I). To determine the percent reduction in emissions when using LEV during reactor cleanout, the following formula was used:

$$\frac{(\text{Concentration without LEV} - \text{Concentration with LEV})}{\text{Concentration without LEV}} \times 100 = \% \text{Reduction}$$

This formula was applied to both filter-based samples as well as particle number concentrations measured with the direct-reading instrumentation. The percent reduction values for three filter-based samples ranged from 75% to 96%, with an average (mean) value of 88% (Table I).

In addition to the filter-based air samples, emission of ENMs was measured with and without LEV, using direct-reading, real-time instrumentation. Similar to the results of the filter-based air samples, the use of LEV reduced particle number concentrations substantially across the entire size range of both instruments (10 nm to 10 μm). Percent reduction values ranged from 78% to 100%, with an average (mean) value of 96% (Table II).

Additional confirmation of the effectiveness of LEV in controlling emissions was noted by examining the TEM images. Filters collected during reactor cleanout while the LEV was operating showed a noticeable decrease in ENM when compared with those collected without the use of LEV (Figure 4). All TEM images, regardless of the use of LEV, indicated that the majority of ENMs existed as agglomerates

TABLE I. Effectiveness of LEV in Reducing Release of Aerosol During Reactor Cleanout Operations: Air Concentrations of Metal Oxides With/Without LEV

Operation	Air Concentration Without LEV ($\mu\text{g}/\text{m}^3$)	Air Concentration With LEV ($\mu\text{g}/\text{m}^3$)	Percent Reduction in Air Concentration Due to Use of LEV (%) ^A
Manganese (Mn) reactor cleanout	3600	150	96
Silver (Ag) reactor cleanout	6700	1700	75
Cobalt (Co) reactor cleanout	710	41	94
Background (reactor area prior to cleanout)	ND	ND	N/A
		Mean (\pm SD)	88 (\pm 12)

Notes: Analytical limit of detection = 1.0 $\mu\text{g}/\text{sample}$.

ND = none detected,

N/A = not applicable,

SD = standard deviation.

^APercent reduction was calculated as follows: [(Without LEV – with LEV) / Without LEV] \times 100.

TABLE II. Effectiveness of LEV in Reducing Release of Aerosol during Reactor Cleanout Operations: Particle Number Concentrations and Percent Reduction Due to LEV

Material	Particle Size Range (nm)	Units of Measure	Measured Concentration			Adjusted Concentration (Without LEV)			Adjusted Concentration (With LEV)		
			Concentration (Without LEV)	Average Background Concentration	(Subtraction of Background) ^A	Concentration (Without LEV)	Average Background Concentration	(Subtraction of Background) ^A	Measured Concentration (With LEV)	Average Background Concentration	(Subtraction of Background) ^A
Silver	300	P/liter	150,684	104,708	45,976	90,909	104,708	0	100		
	500	P/liter	88,872	14,813	74,059	13,721	14,813	0	100		
	1000	P/liter	58,561	4009	54,553	6113	4009	2105	96		
	3000	P/liter	45,108	2097	43,012	4253	2097	2157	95		
	5000	P/liter	28,699	851	27,849	2431	851	1581	94		
	10,000 (10-10000)	P/liter	4597	64	4534	388	64	325	93		
Manganese	300	P/liter	152,058	104,708	47,350	107,766	104,708	3058	94		
	500	P/liter	77,068	14,813	62,255	13,637	14,813	0	100		
	1000	P/liter	62,866	4009	58,858	3738	4009	0	100		
	3000	P/liter	9153	2097	7057	2045	2097	0	100		
	5000	P/liter	9461	851	8611	869	851	19	100		
	10,000 (10-10000)	P/liter	88,328	64	88,265	73	64	10	100		
Cobalt	300	P/liter	29,063	12,146	16,917	13,144	12,146	998	94		
	500	P/liter	189,525	104,708	84,817	93,040	104,708	0	100		
	1000	P/liter	80,892	14,813	66,079	13,520	14,813	0	100		
	3000	P/liter	45,114	4009	41,106	5709	4009	1701	96		
	5000	P/liter	32,032	2097	29,936	3914	2097	1818	94		
	10,000 (10-10000)	P/liter	17,646	851	16,796	2287	851	1437	91		
			1827	64	1764	449	64	386	78		
			25,097	12,146	12,951	14,071	12,146	1925	85		
									Mean (± SD)	96 (± 6)	

Notes: The number concentration of particles in six size ranges (300 nm–10,000 nm) was measured with an ARTI model HHPC-6 optical particle counter and is presented as total particles per liter of air (P/liter) for each size range. The number concentration of particles in the size range (10 nm–1000 nm) was measured with a TSI Model 3007 condensation particle counter and is presented as total particles per cubic centimeter of air (P/cc).

^A Adjusted Concentration = Measured Concentration – Average Background Concentration. If Average Background Concentration exceeds the Measured Concentration, the Adjusted Concentration value is considered to be zero when calculating percent reduction.

^B Percent reduction was calculated as follows: [(Adjusted Without LEV – Adjusted With LEV) / Adjusted Without LEV] × 100.

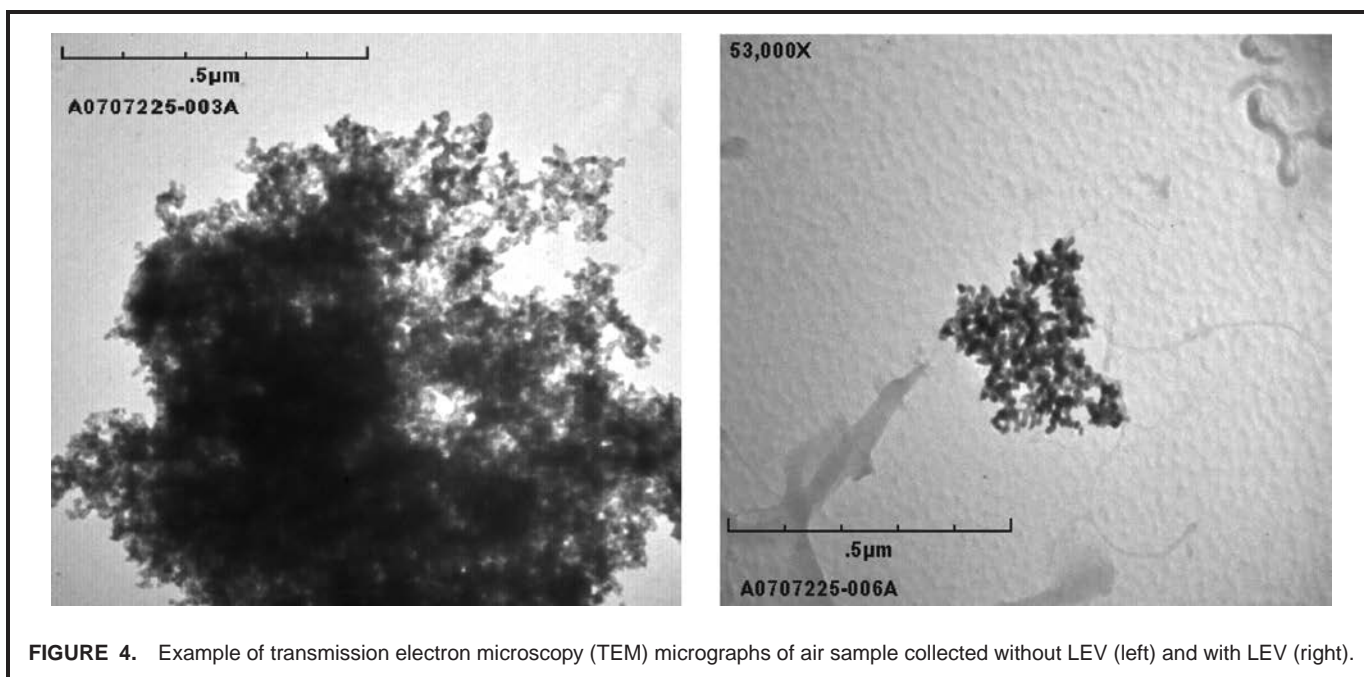


FIGURE 4. Example of transmission electron microscopy (TEM) micrographs of air sample collected without LEV (left) and with LEV (right).

whose size ranged from approximately 500 nm to 2 μm . Elemental analysis confirmed that the agglomerates were composed of the metal oxide of interest.

DISCUSSION

A critical issue when characterizing source emissions and potential exposure using particle number concentration is specificity. Nanoparticles are ubiquitous in many workplaces, originating from sources such as combustion,⁽⁹⁾ vehicle emissions,⁽¹²⁾ and infiltration of outside air. Direct-reading instruments, as used in this evaluation, are generally insensitive to particle source or composition, making it difficult to differentiate between exogenous and process-related nanoparticles. However, short-term elevations in concentrations above the background that coincided with a particular action, process, or task generally may be ascribed to those actions or processes. Fortunately, potential confounders such as forklifts, gas burners, and other combustion sources were not present during this survey.

Clearly, this sampling methodology identified a specific task within a manufacturing process, namely, reactor cleanout, that was responsible for a substantial release of ENMs in this facility. The same methodology was used in an earlier baseline assessment, for the production of a different ENM, with similar success in identifying sources of ENM emissions.⁽⁸⁾ However, this is the first attempt at using this methodology to measure the effectiveness of an ENM emission control technology such as LEV. Others have demonstrated a reduction in nanoparticle exposure (welding aerosol) using a similar LEV system.⁽¹³⁾ In fact, the particle number concentration reduction due to the use of LEV, in combination with a downdraft welding table, was remarkably similar to the reduction presented here

(97–98%). A similar trend in emission reduction was observed for the filter-based air samples (88%) and appears to support the finding that LEV can be used effectively to control emissions of ENMs.

CONCLUSIONS

This study initially was designed to provide a baseline assessment of potential sources of ENM emissions during a variety of handling/process operations. As a result of the initial assessment, the reactor cleanout operation was determined to be an uncontrolled source of ENM emissions, apparently due to technicians brushing and scraping unwanted buildup from the inside of the reactor. This finding prompted an effort to minimize potential worker exposure, mainly through the use of PPE as well as consideration of other measures such as LEV. By expanding the baseline assessment strategy, NIOSH was able to evaluate the LEV system and determine its effectiveness in controlling ENM emissions. By changing the existing reactor cleanout work practice (vigorously brushing and scraping in multiple directions during the February survey) to a more targeted brushing/scraping (toward the inlet of the LEV during the July survey), emissions (both number and mass concentrations) were dramatically reduced.

Despite the large reduction in emissions observed in this study, it is not appropriate to make a determination regarding personal exposures. The air samplers were deliberately placed at a location near the potential source of ENM emission thereby creating a worst case scenario. Therefore, all data collected provide information on process-specific concentrations and should not to be construed as representative breathing zone concentrations. In addition, there are no accepted occupational exposure criteria specific to the engineered nanometer form of

a material against which to compare the findings of this survey. The occupational exposure limits for the larger particulate from each metal could serve as a minimal guide. Despite the limitations imposed on this survey by these factors, it can be concluded that the potential for release of ENMs does exist during reactor cleanout operations. However, based on the analysis of the filter-based air samples and the direct-reading instrumentation, it is clear that a properly maintained LEV can be highly effective in controlling ENM emissions. This finding, coupled with the current use of PPE, appears to be an acceptable method of reducing the potential for worker exposure.

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